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Original
Experimental investigation of the recovery of soaked paper using evaporative freeze drying / Crespi, E.; Capolongo, Antonio; Fissore, Davide; Barresi, Antonello. - In: DRYING TECHNOLOGY. - ISSN 0737-3937. - STAMPA. - 26:3(2008), pp. 349-356. [10.1080/07373930801898141]

Availability:
This version is available at: 11583/1653602 since: 2016-11-17T14:33:52Z

Publisher:
TAYLOR & FRANCIS INC

Published
DOI:10.1080/07373930801898141

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05 May 2023

This is an electronic version of an article published in DRYING TECHNOLOGY, Volume 26, Issue 3, pages 349-356 (2008).

DRYING TECHNOLOGY is available online at:

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Experimental investigation of the recovering of soaked paper using evaporative freeze-drying

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Abstract

The aim of this paper is to develop an experiment and a procedure to investigate the restoration of water-damaged paper and archival materials using freeze-drying in order to allow a reproducible test and comparison of the influence of different operating conditions on drying time and restored paper quality. Firstly, a reproducible method for the preparation of soaked samples simulating water-damaged paper has been developed. Then, the samples have been freeze-dried in a laboratory scale apparatus which allowed monitoring the temperature as well as the weight of the samples; the technique of evaporative freezing, which reduces the drying time required, has been used in this case. An innovative procedure for the visualization of the progress of the drying process has been validated, thus allowing the validation of a simple phenomenological model of the time evolution of the ice core volume; in addition, data on the residual moisture of the dried paper sheets in different zones have been given. Finally, optimization of this particular drying process by using simple or more sophisticated approaches has been discussed.

Keywords

Freeze-drying, evaporative drying, vacuum drying, water-damaged documents, archival materials restoration.

Introduction

Today there is a growing interest in finding an effective method for the preservation and the recovery of soaked archival and librarian materials. Water-damaging of paper can be due to different causes: direct ones, including floods, torrential rains, breaking of hydraulic or conditioning systems and indirect ones, as a consequence of fire extinguishment. In both cases, the main damages produced by water are absorption and swelling, cockling, microbiological infection, adhesion of leaves, migration of inks and dyes, distortion (McCleary, 1987). Manual recovery can give good results but with high costs and the process is very slow; thus, different drying methods as vacuum drying, freeze-drying, microwave and extraction with solvent have been proposed in the past (Flink and Hoyer, 1971; Flink, 1972; Flink et al., 1977; Thomas and Flink, 1975; Cunha, 1977; Fischer, 1977; Sugarman and Vitale, 1992).

Freeze-drying is a two steps process: firstly, the product is frozen, and thus the degrading processes caused by the free water is stopped; then, the ice is removed by sublimation. The use of this technique allows to process a large amount of wet material without further damages and can be economically advantageous in comparison to manual recovery. Unfortunately, in many cases, there is not an appropriate dialogue between scientists and paper conservators. Scientists do not know the restoring techniques and the related problems and paper conservators have not the necessary knowledge of physics and engineering to find the best process for a material. For this reason, the trial and error method is still widely employed in this field.

The present work has the following aims:

1) setting a standard and reproducible method to prepare soaked homogeneous

samples; this step is necessary to assess the validity of the proposed procedure and to compare in a reproducible way the influence of different operating conditions on drying time and restored paper quality, but has been quite often neglected in past works in this field;

2) setting an experimental approach to analyze the sublimation phase inside the paper sample during the freeze-drying;
3) applying freeze-drying to water-soaked samples to restore the dried condition; the data will be valuable to highlight real behaviour in evaporative drying and to validate modelling results;

A simple model is employed in this work to predict the time evolution of the frozen core in the sample and to show how off-line simulation can be used to optimise the operation and minimize process duration and costs.

Experimental procedure

Materials

Modern blank paper, size A4, 80 g/m^2 (produced by Burgo, San Mauro Torinese, Italy) is used. Reams are cut to obtain sheets with dimension of 42 mm x 59 mm. A single sample of paper consists of a little block of sheets (weight: 18 g ÷ 18.30 g; number of sheets: 100; height: about 10 mm).

Preparing reproducible soaked paper

The whole procedure is divided into three steps:

- conditioning of dry samples at controlled temperature (27°C) and relative humidity (43.16%), according to the suggestions of Greenspan (1977): the paper sheets are placed on the ceramic support of a laboratory drier

containing an aqueous solution of potassium carbonate that allows maintaining the desired conditions of humidity;

- soaking in distilled water at 27°C for 18 hours;
- drainage: the soaked samples are placed for 5 hours in a box where the atmosphere is saturated with water vapour and allowed to drain.

This procedure is similar to that proposed by Capolongo and Barresi (2004): a new experimental apparatus is used to overcome or, at least, to reduce some technical difficulties and problems connected with an accurate acquisition of the data. The new apparatus (Figure 1) consists of a plastic cylinder half filled with distilled water and closed with a cover. The samples are put in four little cages (70 x 25 x 50 mm) stuck on the cover; the cages held the samples in position without pressing. By overturning the cylinder it is possible to make alternately soaking and drainage in saturated air in this same apparatus. To avoid sheet raising during the drying, a wire net (12 mm mesh) is used to cover every single block; the dimensions of the wire does not affect mass transfer from the paper.

Visualization of the dry paper-ice interface during freeze-drying

A paper sample partially dried presents dried external sheets and an internal core still frozen. In order to evidence the progress of the drying and to obtain data for model validation it is important to fix and evaluate the position of the interface at different times. In the proposed method a dye is used to visualize the two zones quickly and permanently; to do this we need:

- a liposoluble dye with a good definition on paper and photostatic (Sudan Blue II);
- an apolar solvent able to dissolve the dye and with a low vapour pressure (Exan);

- in order to obtain reliable data, of course, the contour of the ice core must correspond exactly to that of the coloured zone. In order to verify this, in a test run the real ice/paper interface has been substituted by a similar wax/paper interface obtained dissolving a little amount of wax on a sheet.

To summarize the general procedure consists of:

- stopping the freeze-drying cycle at a fixed time;
- immersing the sample in the colouring hexane solution for a few seconds;
- complete the freeze-drying cycle;
- observing and scanning the sheets.

Freeze-drying experiments

Freeze-drying is carried out in a laboratory freeze-dryer (Lyobeta 25, Telstar Industrial S.L., Spain). The guaranteed performances are:

- condensing capacity up to 8 kg of ice in 24 hours;
- minimum temperature in the condensation chamber equal to –80°C;
- minimum pressure of $2 \cdot 10^{-2}$ mbar in the drying chamber.

The freeze-dryer is interfaced to a computer to acquire in real time the values of the pressure in the drying chamber, the temperature and the mass of the samples. Soaked samples are dried through "evaporative drying", a process consisting of a rapid decrease of the pressure which causes a rapid liquid evaporation and thus freezing. This type of procedure can be advantageous because it does not require to freeze the sample, thus reducing the energy consumption of the process, and it eliminates quickly a fraction of water; some care must be taken to avoid surface damaging (Barresi et al., 2003).

The operation is carried out using a shelf temperature of 20°C and a chamber pressure of 0.3 mbar. During the freeze-drying process, the following parameters are monitored:

- pressure, using a Pirani gauge;
- product temperature, employing three thin unshielded Constantan thermocouples (type T) placed on the top (below the first sheet, h=1), in the middle (h=1/2) and at the bottom of the sample (upon the last sheet, h=0);
- mass of the sample.

Mass measurement is very important to establish the drying kinetics and is studied in two ways:

1) using off-line measurement, i.e. stopping freeze-drying cycles at different times (before complete drying is obtained) and then weighing the samples to evaluate the amount of water sublimated; at the same time, using the procedure previously described, it is possible to evidence the shape and the size of the frozen core and to evaluate the residual moisture in the top and bottom sheets;
2) using in-line measurement, thanks to a special balance (Vallan et al., 2005; Vallan, 2007) placed in the drying chamber. Conventional electronic balances are not conceived to work inside a freeze dryer, at low temperature and under vacuum; moreover, the measure can be affected by several disturbances, like buoyancy effects, vibrations, gas flows and temperature gradients. Finally, a balance can weigh a reduced amount of substance, that can be not representative of the full process and the balance itself can alter the behaviour of the sample. The balance used in this work employs a mechanical lifting system to rise - and then release - the sample when the mass measurement has to be carried out. The mass measurement is obtained by means of a general purpose load cell that is connected between the moving plate and the lifting system. This solution is effective as it does not affect significantly the average heat transferred by conduction, even if a special attention has to be paid in order to maintain unchanged the heat

exchanged by radiation. This represent a remarkable innovation with respect to other available devices, that require to remove the sample using a manipulator or that alter the thermal transfer between the shelf and the weighed samples. The original design of the balance has been modified as the balance has to weight blocks of papers and not vials: to this purpose, the samples are now placed over a plate connected to the lifting system. The balance has a range of 2 kg, a mass resolution of few milligrams and an uncertainty of few tens of milligrams over a wide range of temperatures (-40 °C, +40 °C).

After the freeze-drying process, it is possible to leaf through the sample.

Results and discussion

Preparing reproducible soaked paper

Soaking tests are carried out to determine an adequate soaking time in order to adsorb the maximum amount of water. Figure 2 shows the time evolution of the amount of adsorbed water by a conditioned dry sample in the old apparatus (Capolongo and Barresi, 2004) and in the new one. The comparison of the two series of data evidences the improvements obtained with the new experimental apparatus: the experimental error is reduced, the saturation is reached after 8 hours and the system exhibits a better stability. These results and the better reproducibility can be explained because the new apparatus reduces the manipulation of the samples. Experimental results have evidenced that in order to get good and reproducible results it is important to avoid the presence of small gas bubbles: air represents an obstacle to water absorption by the samples. In Table 1 it is possible to see the final values of adsorbed water

obtained with the two apparati considered: the amount is increased when the sample is agitated, thus allowing the release of air. In this conditions reproducible soaked samples are obtained: the amount of adsorbed water is 22.42 ± 0.78 g corresponding to 123.8 ± 4.7 % related to the initial dry weight.

Visualization of the dry paper/ice interface during freeze-drying

A preliminary set of experiments has been carried out in order to test the proposed procedure for the determination of the dry paper/ice interface during freeze-drying; in particular, the aim of this test is to verify if significant dye diffusion can take place in the sample, thus altering the determination of the interface. The ice core has been simulated using a wax spot which creates a transparent spot that can be easily detected on a dry paper. The sample is firstly immersed in water and then in the dye solution: the wax is insoluble in water and the liposoluble dye can colour only the wax spot. In this way it is possible to visualise and determine the geometry before and after the colouring treatment and thus to make a comparison: if the two spots are superimposed it is possible to see that the dye colours exactly the wax spot and does not create any artefacts on the paper sample. The good results obtained can be observed in Figure 3: a well-defined interface and an effective sample tomography are obtained.

The possibility of visualising the ice shape (and consequently the drying kinetics of the sample) in a permanent way is of paramount importance. After the freeze-drying is stopped and the samples are treated with dye which colours the part at least partially dried, while the zone corresponding to the still frozen core remains blank. After completion of the drying, the sheets of the paper block are examined; the central one is shown in Figure 4 at different drying times. Looking at the images obtained we can appreciate how the ice

core shrinks progressively. In particular it is important to underline that the ice core inside the paper block maintains initially a rough rectangular shape, confirming previous literature data (Carapelle et al., 2001; 2002) and only toward the end of primary drying rounds off. Thanks to this method, we can also identify the end of primary drying and of the whole process. In fact, according to mass and temperature values, ice is still present after 14 hours, while after 16 hours samples are completely dried.

Application of the freeze-drying process

Soaked samples processed by evaporative drying are completely dried in 16 hours. In Figure 5 the temperature profiles of shelf and product during the process are shown: these measurements confirm that the product temperature at h=0 and h=1, i.e. at the bottom and at the top of each sample, are higher than at h=1/2 because external ice sublimates quicker than the internal one. It is important to highlight that lyophilisation can occur also from the bottom of the sample, as sublimation is allowed. We can also estimate accurately the end of primary drying because there the curve presents a point of inflection and, after this, the temperature increases very quickly. For h=0 and h=1 this sudden change in temperature takes place in the first hour of process while the values monitored by the thermocouple in the middle of the sample mark the end of the primary drying after 16 hours.

As well as temperature, the mass is measured in real time using a balance inside the freeze-dryer chamber. The curve (Figure 6) is compared with data obtained using off-line measurements and evidences good agreement between the two series of data. In the first hour of the process a great quantity of water is removed quickly; then, a progressive decrease of the sublimation rate is observed. This is justified considering that the dried layer constitutes a mass

transfer resistance, which is an obstacle to the passage of the water vapour. After 14 hours the sample mass is comparable to the conditioned dry one but, in reality, an ice core can still be found inside the paper block. The contemporaneous development of primary and secondary drying makes external sheets completely dried while the core is still frozen: the core sublimates but the extremities over-dry. After 16 hours a completely dried sample can be obtained (the final residual humidity equal to 1.2±0.3 %).

The results indicate the necessity of reconditioning the dried paper to re-establish the right value of humidity (in conditioned dry paper is about 4-5%). So it is interesting to evaluate the humidity distribution inside the sample. The paper block is divided into three layers: the core still frozen and the two extremities completely dried. For every layer the humidity (by gravimetrical method) and the number of dried sheets are measured in order to have more information about the drying kinetics of soaked paper. The data are shown in Figures 7 and 8: the values decrease while time passes, with the sheets in the upper layer showing a humidity percentage inferior to the sheets which are in contact with the plate surface. Just after 1 hour since the start of the drying it is possible that over-drying occurs in the upper sheets (4% of humidity compared to 5% that is the normal amount of water in conditioned dry paper), while over-dying occurs in 4 hours for the sheets in the lower layer; the final average humidity value is equal to 0.6 ± 0.03 %, after 20 hours of drying. As a consequence of simultaneity of primary and secondary drying, the experimental results suggest that it is difficult to interrupt freeze-drying in order to obtain completely dried paper having a 4-5% of residual moisture. Over-drying is unavoidable and reconditioning is recommended before handling, especially in case of antique documents and those containing miniatures and paintings.

Modelling and process optimization

An extended experimental investigation is required in order to point out the influence of the various operating conditions on the results that can be obtained (in particular on the time required to complete the primary drying), but it is time consuming, expensive and it is not the main goal of this work. In the literature about freeze-drying it is possible to find a lot of papers discussing the role of the various operating parameters (namely shelf temperature and chamber pressure) of a drying process and the result is that the optimal value of these parameters is generally dependent on the particular case under investigation. Thus, mathematical modelling can be a useful tool to obtain the optimal working conditions.

A detailed three-dimensional model should be used because of the sample geometry, but the numerical solution can be time consuming and it is extremely difficult to write adequate boundary conditions for the balance equations. Thus, the simple phenomenological model of Carapelle et al. (2001) has been used to mathematically describe the experimental results. The model describes the loss of ice content in the sample as a function of time: after a short initial period where quick evaporation occurs, the ice core inside the sample sublimates. This is a slow process, mainly ruled by heat transfer within the sample. The main hypothesis of the model are:

- the ice core has the same shape and the same proportions of the original sample during the process and it remains at the centre of the sample;
- the heat flux is proportional to the area of the core surface facing the heating plate and to the inverse of the distance between the core and the heating plate;
- the thermal conductivity of the paper is proportional to its density (Nederveen and Finken, 1992).

The details of the calculations can be found in Carapelle et al. (2001) and are reported in the Appendix. Figure 4 compares the interface between the ice core and the dried paper obtained at various times during the evaporative drying process with the predictions of the model, evidencing the good agreement; similarly, Figure 6 compares the experimental values of the sublimated mass with the predictions of the model, thus demonstrating the adequacy of the model to describe quantitatively the process, even if, due to the simplifications of the model, in the first half of the drying period the amount of sublimated mass is overestimated.

The time required to complete the sublimation of the ice core is a function of the dimensions of the sample, of the thermal conductivity of the paper and of the temperature difference between the ice core and the heating plate (ΔT). While the volume of the sample, as well as its thermal conductivity, cannot be manipulated as they depend on the material that we would like to dry, we can use ΔT, and thus the temperature of the heating plate, to optimize the process, taking into account that there is a maximum value that should not be overcome in order to avoid paper damaging (a value of 30°C can be considered a safe limit for most common type of papers). Also the pressure of the chamber should be optimized: low values of the pressure increase the driving force for the mass flux, but too low values can have an opposite effect, due to the reduction of the heat transfer from the shelf to the paper. The simplified model of Carapelle et al. (2001) does not allow for such investigation and thus, in this work, a constant value of chamber pressured has been considered.

Figure 9 shows the time required to complete the sublimation of the ice in a sample (having the dimensions of the paper investigated in this work) as a function of its thermal conductivity (that can change depending of the characteristics of the paper) and of ΔT; the values of the conductivity that are

used to calculate the curves of Figure 9 are typical of wet paper samples (Nederveen and Finken, 1992). A chart like this can be easily calculated by means of the simplified model of Carapelle et al. (2001) and can thus be used to find out the optimal working conditions for the process. These curves are obtained for our sample. Shorter time interval are required if the sample is small, thus, in real case of wet paper, it is preferable to freeze the papers in several small packages than in one large sample. The practical recommendation for paper conservators is to separate the damaged paper as much as possible before freezing.

Conclusions

The present work aims to show a full procedure for the investigation of an industrial process for drying soaked samples:

i) a simple and economic method for preparing reproducible soaked samples of paper has been defined;

ii) an effective method to show the ice shape in the samples during freeze-drying has been assembled in our laboratory. A liposoluble dye, employed in the tests, puts in evidence the geometry of the ice core and its evolution during freeze-drying. This result is very important because it allows the visualization of the ice sublimation and it gives useful information about the ice quantity in a certain time instant;

iii) evaporative drying has been demonstrated to be effective in completely drying the soaked paper without excessive damaging.

Moreover, as a consequence of simultaneity of primary and secondary drying and the short duration of the latter, the results obtained suggest that it is

difficult to interrupt the drying process in order to get dried paper having a desired 4-5% residual moisture condition. Referring to antique documents, especially those containing miniatures or paintings, conditioning of brittle dried paper is recommended before handling.

Acknowledgements

The authors would like to thank Dr. Francesca Bosco and Dr. Mauro Banchero (Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Italy) for fruitful discussions and technical assistance.

References

Barresi A. A., Capolongo A., Rovero G. (2003). Soaking and freeze-drying of paper simulating water-damaged documents for salvage of archival materials. Proceedings of "ECCE4, 4th European Congress of Chemical Engineering", 21-25 September, Granada, Spain, vol.8, paper O-8.4-006.

Capolongo A., Barresi A. A. (2004). Freeze-drying of water-damaged paper material. Restaurator, 25(2), 119-128.

Carapelle A., Henrist M., Rabecki F. (2001). A study of vacuum freeze-drying of frozen wet papers. Drying Technology, 19(6), 1113-1124.

Carapelle A., Henrist M., Rabecki F. (2002). Restoration of flooded documents: past and future activities. Proceedings of "Lyophilization and Freeze-Drying Conference 2002", Amsterdam, October 19-25.

Cunha G. M. (1977). An evaluation of recent developments for the mass drying of books. In: Preservation of paper and textiles of historic and artistic value, ed. John C. Williams. Advanced in Chemistry Series, 164. Washington: American Chemical Society: 95-104.

Fischer D. J. (1977). Simulation of flood for preparing reproducible water damaged books and evaluation of traditional and new drying processes. In: Preservation of paper and textiles of historic and artistic value, ed. John C. Williams. Advanced in Chemistry Series, 164. Washington: American Chemical Society, 105-123.

Flink J. M. (1972). Utilisation of freeze-drying to save water-damaged manuscripts. Vacuum, 22: 273.

Flink J. M., Hoyer H. (1971). The conservation of water damaged written documents by freeze drying, Nature, London, 234(5329), 420.

Flink J. M., Juszczak L. J., Goding D. P. (1977). Application of novel drying

techniques for conservation of water soaked documents, AIChE Symposium Series, 73(163), 148-156.

Greenspan L. (1977). Humidity fixed points of binary saturated aqueous solutions. Journal of Research of the National Bureau of Standards A: Physics and Chemistry 81A1, 89-96.

McCleary J. P. (1987). Vacuum freeze-drying, a method used to salvage water-damaged archival and library materials: a RAMP study with guidelines. Prepared by J. McCleary for the General Information Programme and UNISIST. - Paris: Unesco, PGI-87/WS/7.

Nederveen C. J., Finken J. G. M. (1992). Thermal conductivity measurements on wet paper samples at high temperatures. Drying Technology, 10(1), 189-198.

Sugarman J. E., Vitale T. J. (1992). Observations on the drying of paper: five drying methods and the drying process. Journal of the American Institute of Conservation, 31(2), 175-197.

Thomas D., Flink J. M. (1975). Rapid drying of water soaked books using a microwave tunnel dryer. Restaurator, 2, 105-119.

Vallan A. (2007). A measurement system for lyophilisation process monitoring. Proceedings of Instrumentation and Measurement Technology Conference - IMTC 2007 Warsaw, Poland, May 1–3.

Vallan A., Parvis M., Barresi A. A. Sistema per la misurazione in tempo reale di massa e temperatura di sostanze sottoposte a liofilizzazione. Italian Patent n° BO2005A000320, 2005.

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Figure 8 Residual moisture distribution in the part of the sample that has completed primary drying.

Figure 9 Influence of the temperature difference between the ice core and the heating plate (ΔT) on the time required to complete the sublimation of the ice core for various values of the thermal conductivity of the wet paper (model predictions).

Appendix - Details of the calculations made using the phenomenological model by Carapelle et al. (2001)

If X, Y and Z are the dimensions of the sample and x, y and z are the dimensions of the ice core, the variation of the dimensions of the ice core is given by:

$$\Delta X = \frac{X}{2} - \frac{x}{2}, \quad \Delta Y = \frac{Y}{2} - \frac{y}{2}, \quad \Delta Z = \frac{Z}{2} - \frac{z}{2} \tag{1}$$

due to the hypothesis that the ice core remains at the centre of the sample. As the ice core has the same shape (and thus the same proportions) of the original sample, we can write:

$$R_{ZX} = \frac{Z}{X} = \frac{z}{x}, \quad R_{YX} = \frac{Y}{X} = \frac{y}{x} \tag{2}$$

Therefore:

$$z = xR_{ZX}, \quad y = xR_{YX} \tag{3}$$

The heat flux reaching the ice core is given by:

$$\frac{\Delta Q}{\Delta t} = -kS\frac{\Delta T}{\Delta Z} \tag{4}$$

where:

- ΔQ is the amount of heat transferred (J)
- Δt is the time interval (s)
- ΔT is the temperature difference between the heating plate and the ice core (K)
- ΔZ is the distance between the heating plate and the ice core (m)
- k is the thermal conductivity of the paper (W $m^{-1}K^{-1}$)
- S is the area of the base surface, given by:

$$S = xy = x^2 R_{YX} = 4R_{YX}\left(\frac{X}{2} - \Delta X\right)^2 \tag{5}$$

As a consequence, the heat flux can be calculated as:

$$\frac{\Delta Q}{\Delta t} = -8k\Delta T \frac{R_{YX}\left(\frac{X}{2}-\Delta X\right)^2}{Z-\left[2R_{YX}\left(\frac{X}{2}-\Delta X\right)^2\right]} \tag{6}$$

Thus, the time required to sublimate 1 g of ice is given by:

$$t = L\frac{Z-\left[2R_{YX}\left(\frac{X}{2}-\Delta X\right)^2\right]}{-8k\Delta T R_{YX}\left(\frac{X}{2}-\Delta X\right)^2} \tag{7}$$

where L is the latent heat of sublimation of ice (J g^{-1}).

Let us call now V the volume of the ice core at a given time t; at the time t' the ice core will have lost one gram of ice and the volume will be V', where:

$$V - V' = \rho^{-1} \tag{8}$$

where ρ is the density of ice (g m^{-3}). From eq. (1) - (3) it comes that:

$$x^3 R_{YX} R_{ZX} - x'y'z' = \rho^{-1} \tag{9}$$

and, as the ice core keeps the same shape and the same proportions as the original sample, we can write:

$$R_{YX}R_{ZX}\left(x^3 - x'^3\right) = \rho^{-1} \tag{10}$$

being $z' = R_{ZX}x', y' = R_{YX}x'$. Let us call now $\Delta x = \frac{x-x'}{2}$. We can write:

$$\frac{x}{2} = \Delta x + \frac{x'}{2} \tag{11}$$

If $\Delta X'$ is the position of the ice core at time t', we have:

$$\Delta x = \Delta X' - \Delta X \tag{12}$$

where Δx is the increment of the coordinate x of the ice core when the time increases from t to t'. From eq. (11) we have:

$$x' = 2\left(\frac{x}{2} - \Delta x\right) \tag{13}$$

that, combined with eq. (11), gives:

$$\Delta x = \frac{x}{2} - \frac{1}{2}\sqrt[3]{x^3 - \frac{1}{R_{YX}R_{ZX}\rho}} \tag{14}$$

and, using eq. (1) and (12), we have:

$$\Delta X' = \frac{X}{2} - \frac{1}{2}\sqrt[3]{8\left(\frac{X}{2} - \Delta X\right)^3 - \frac{1}{R_{YX}R_{ZX}\rho}} \tag{15}$$

Thus, using eq. (7) and (15) in an iterative way we can calculate the time needed to sublimate each gram of ice and the position of the ice core after this sublimation.

Table 1

Time, h	% adsorbed water	
	Previous apparatus (Capolongo and Barresi, 2004)	**This work**
2	52.53 ± 8.97	55.31 ± 8.31
3	60.07 ± 13.85	74.95 ± 4.19
4	43.65 ± 2.58	103.36 ± 4.94
5	64.59 ± 24.80	109.29 ± 11.59

Figure 1

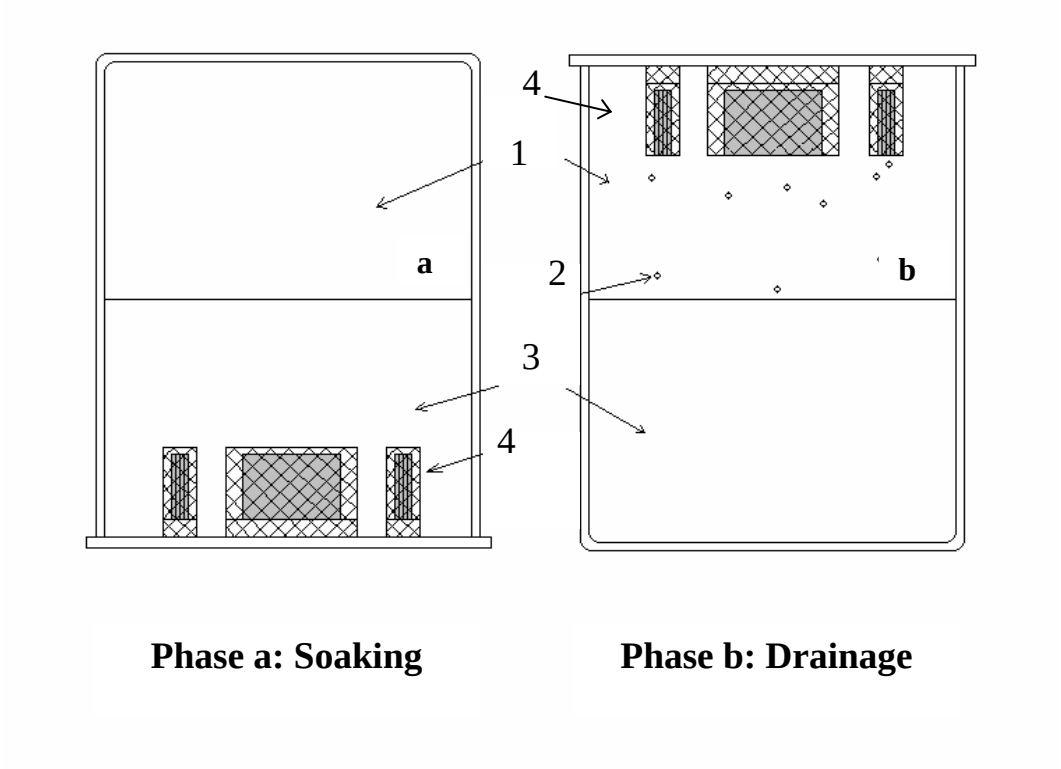


Figure 2

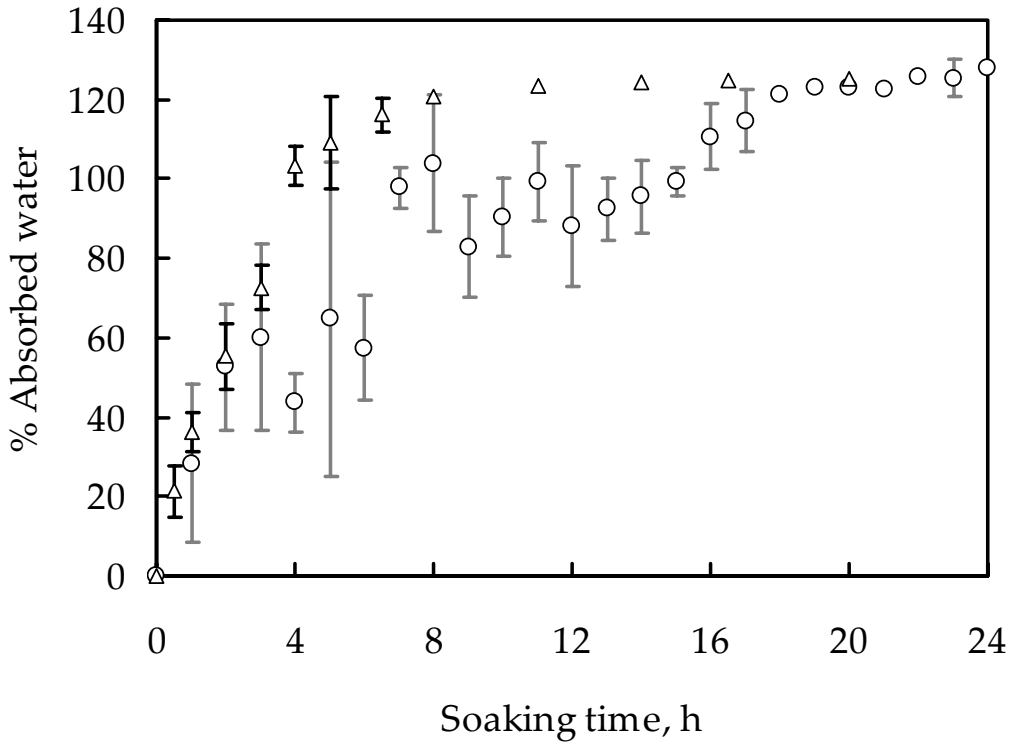

140
120
100
80
60
40
20
0
% Absorbed water
0
4
8
12
16
20
24
Soaking time, h

Figure 3

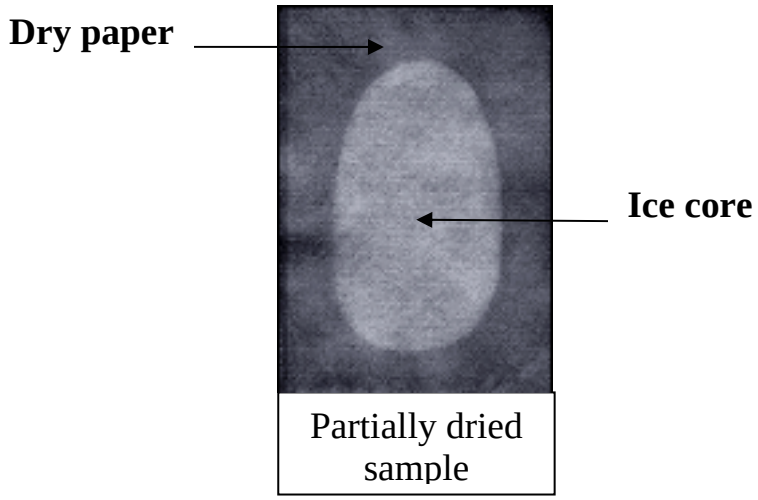


Figure 4

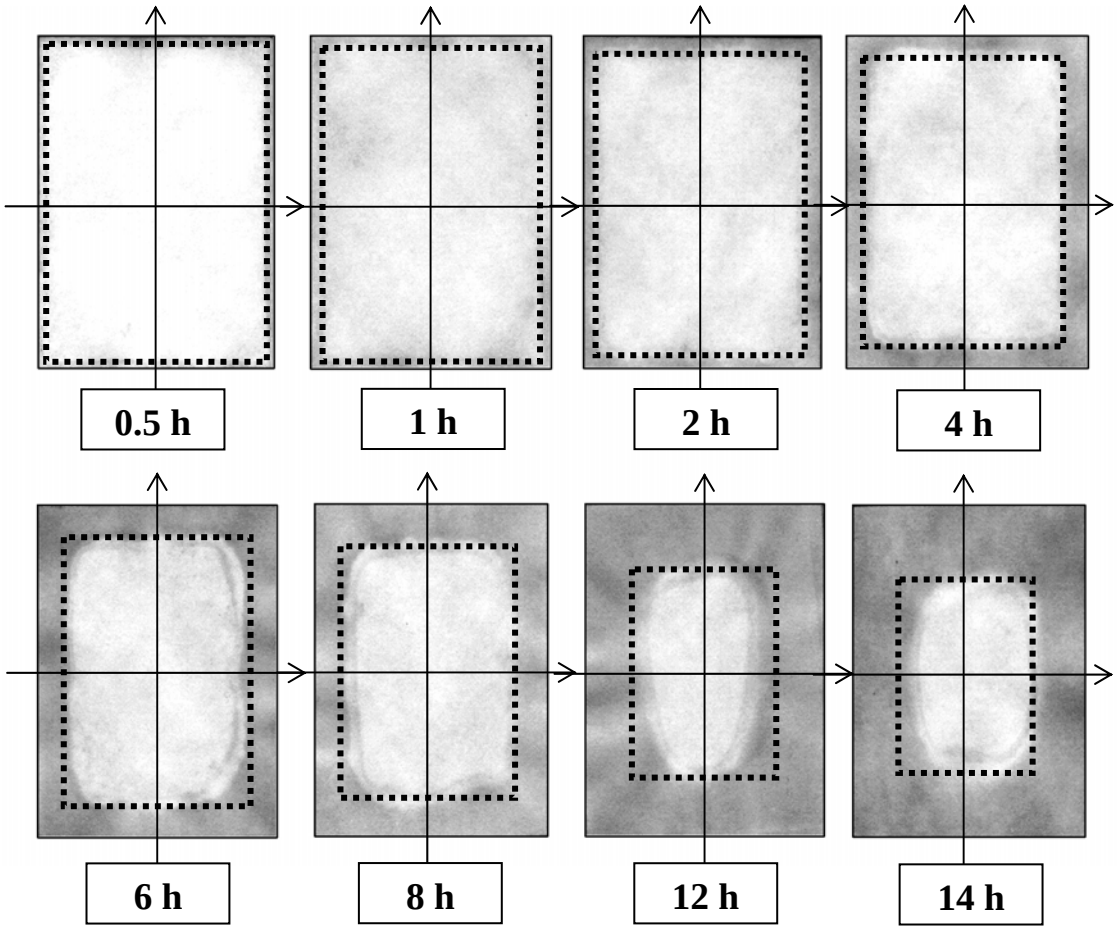


Figure 5

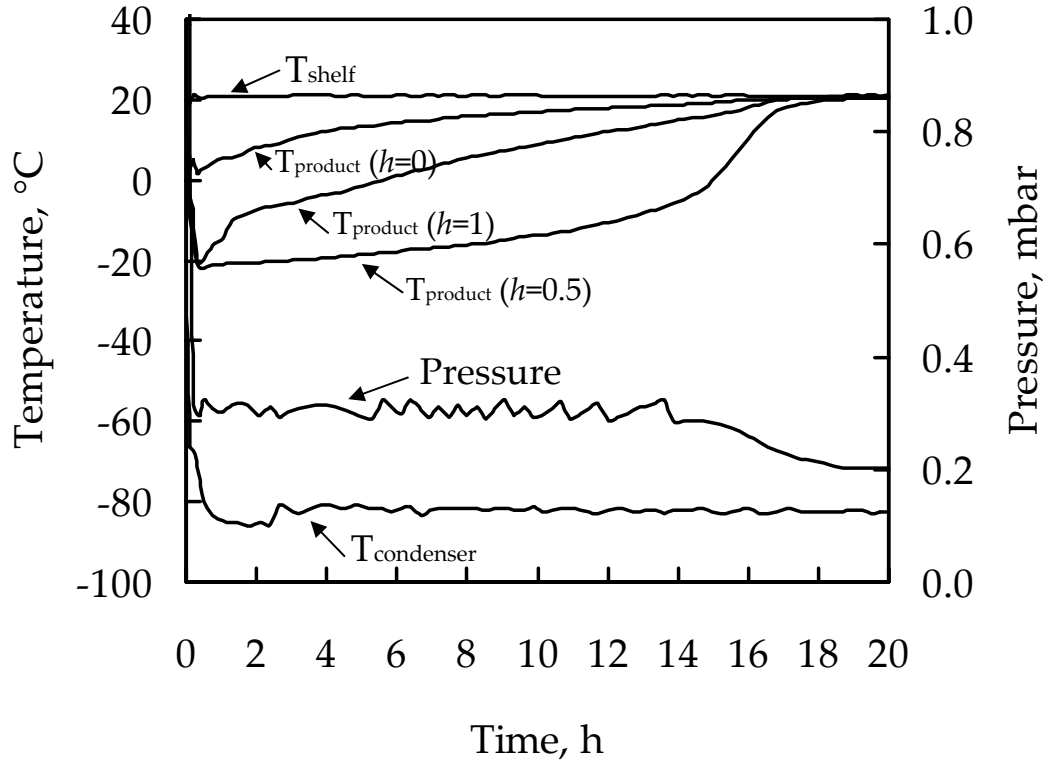

40
20
0
-20
-40
-60
-80
-100
1.0
0.8
0.6
0.4
0.2
0.0
0 2 4 6 8 10 12 14 16 18 20
Time, h
Temperature, °C
Pressure, mbar
Tshelf
Tproduct (h=0)
Tproduct (h=1)
Tproduct (h=0.5)
Pressure
Tcondenser

Figure 6

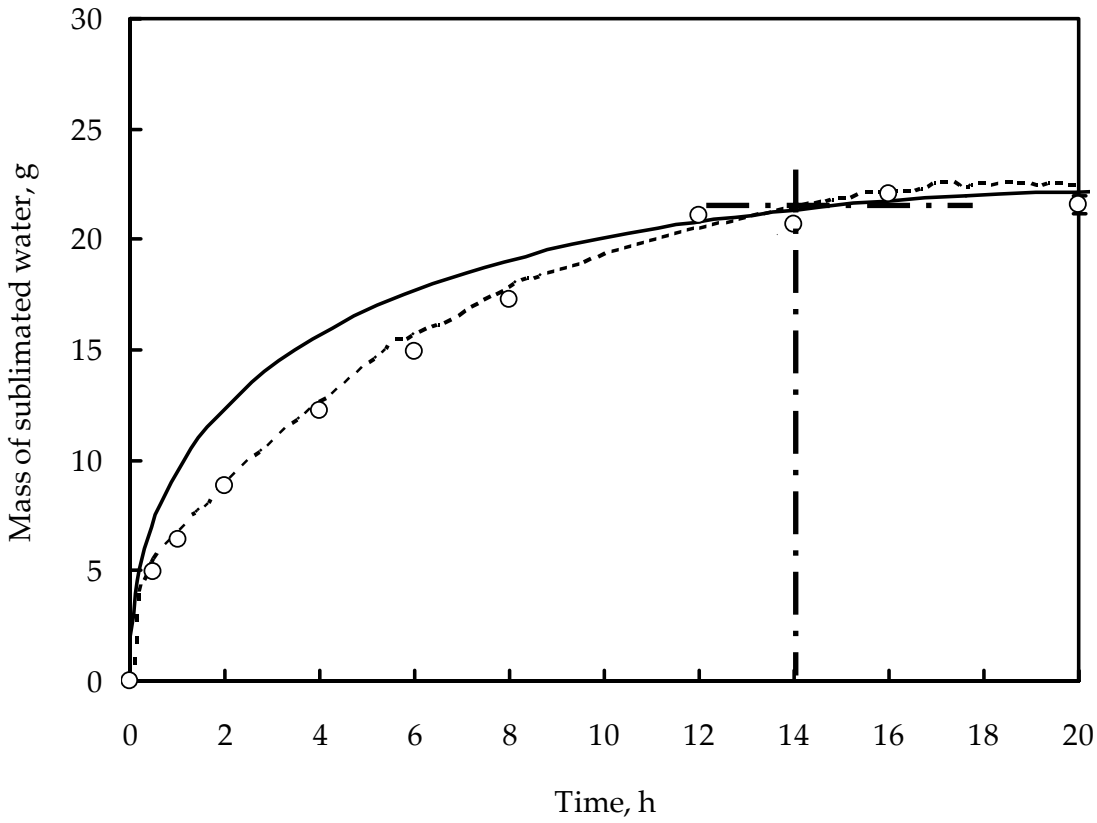

Mass of sublimated water, g
30
25
20
15
10
5
0
0
2
4
6
8
10
12
14
16
18
20
Time, h

Figure 7

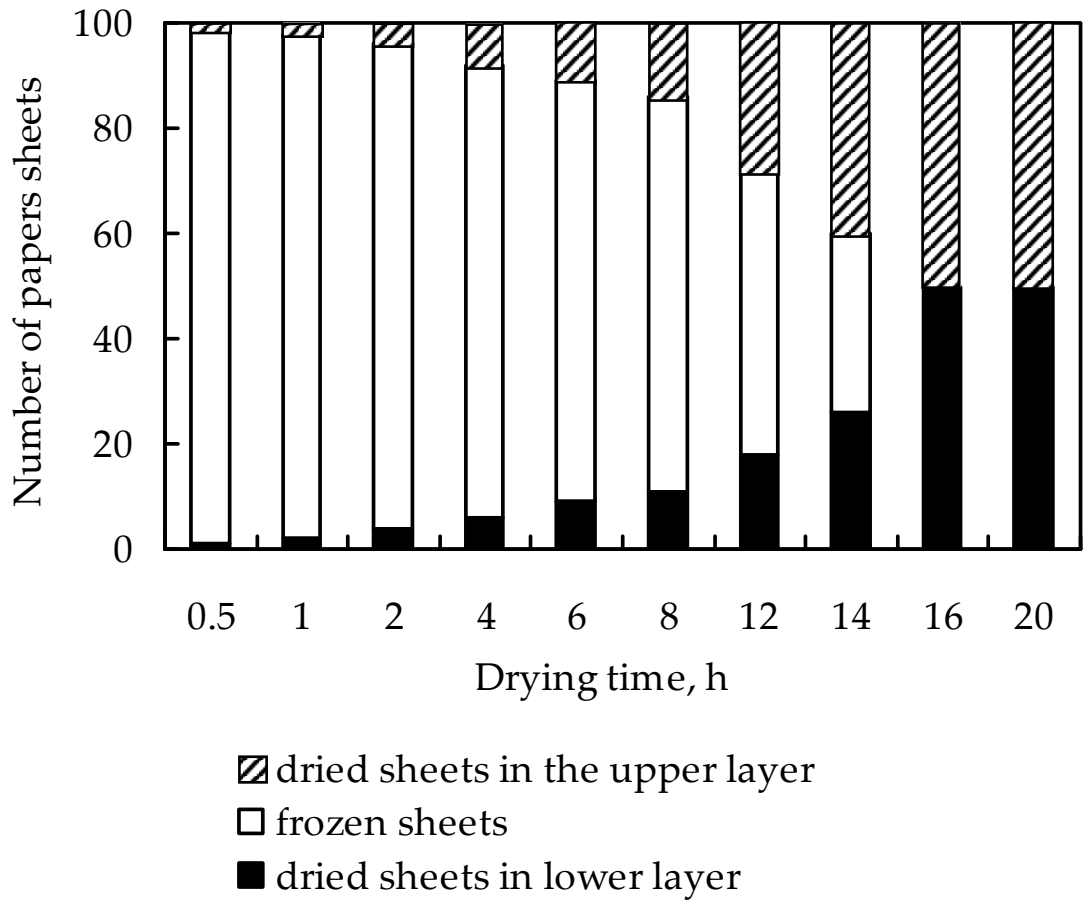

100
80
60
40
20
0
Number of papers sheets
0.5
1
2
4
6
8
12
14
16
20
Drying time, h
dried sheets in the upper layer
frozen sheets
dried sheets in lower layer

Figure 8

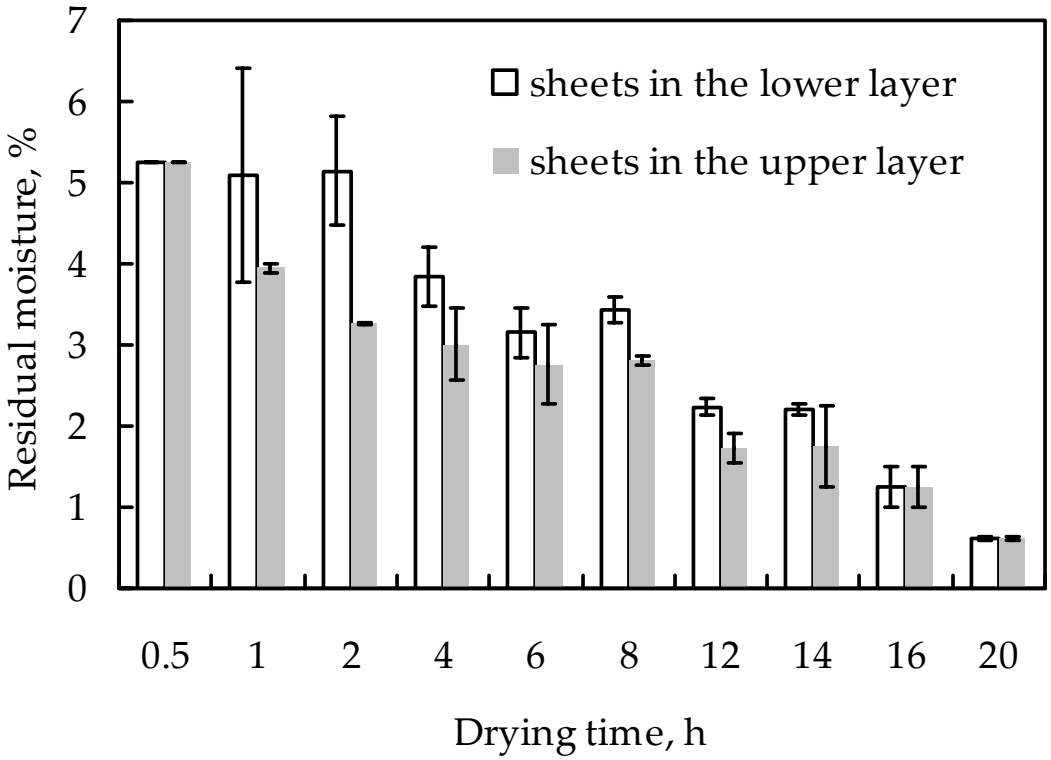
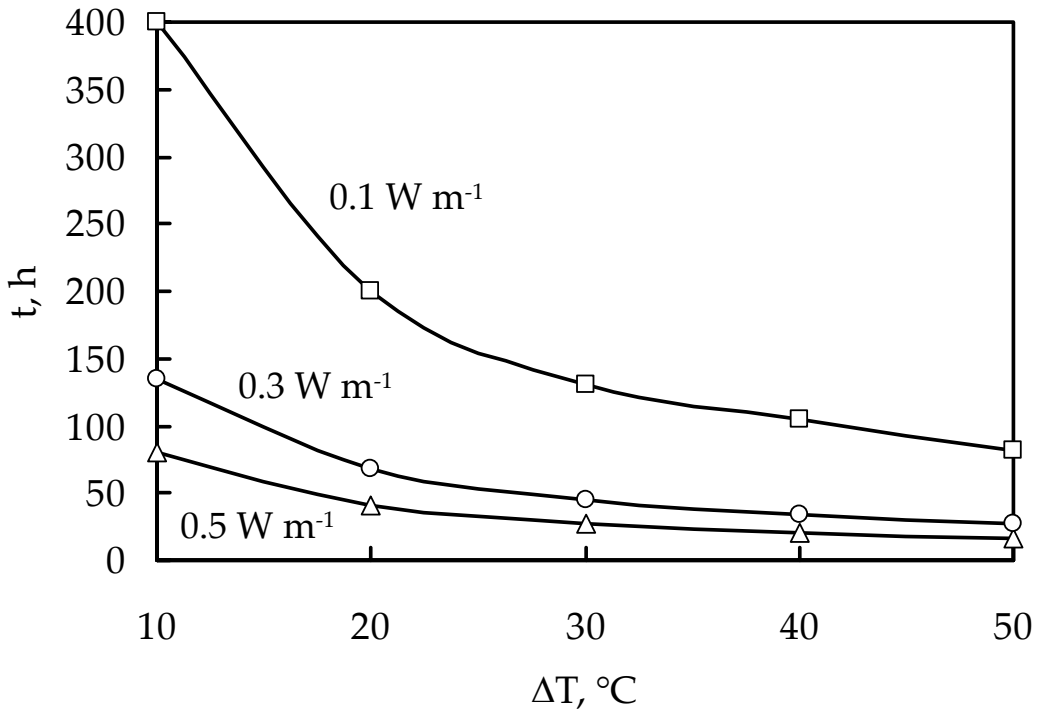

Residual moisture, %
7
6
5
4
3
2
1
0
sheets in the lower layer
sheets in the upper layer
0.5
1
2
4
6
8
12
14
16
20
Drying time, h

Figure 9


400
350
300
250
200
150
100
50
0
t, h
0.1 W m-1
0.3 W m-1
0.5 W m-1
10
20
30
40
50
ΔT, °C